

## CLAIMS

- Sub B* 1. Use as foaming agents having a low environmental impact of azeotropic or near azeotropic compositions, based on difluoromethoxy-bis(difluoromethyl ether) and/or 1-difluoromethoxy-1,1,2,2-tetrafluoroethyl difluoromethyl ether, essentially consisting of:

	composition % by weight
I) difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); n-pentane	1-95 99-5
II) difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); iso-pentane	1-99 99-1
III) difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); dimethyl ketone (acetone)	1-60 99-40
IV) difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); 1,1,1,3,3-pentafluorobutane ( $\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3$ , HFC 365 mfc)	1-99 99-1
V) difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); 1,1,1,4,4,4-hexafluorobutane ( $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ , HFC 356 ffa)	1-40 99-60
VI) difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); methoxymethyl methylether	1-96 99-14
VII) difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); n-hexane	30-99 70-1
VIII) 1-difluoromethoxy	

	1,1,2,2-tetrafluoroethyl difluoromethyl ether ( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ ); n-pentane	1-93 99-7
IX)	1-difluoromethoxy 1,1,2,2-tetrafluoroethyl difluoromethyl ether ( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ ); dimethyl ketone (acetone)	30-99 70-1
X)	1-difluoromethoxy 1,1,2,2-tetrafluoroethyl difluoromethyl ether ( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ ); n-hexane	15-99 85-1
XI)	1-difluoromethoxy 1,1,2,2-tetrafluoroethyl difluoromethyl ether ( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ ); ethyl alcohol	5-99 95-1

2. Use of azeotropic or near azeotropic compositions  
according to claim 1 essentially consisting of:

		composition % by weight
I)	difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); n-pentane	25-95 75-5
II)	difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); iso-pentane	25-98 75-2
III)	difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); dimethyl ketone (acetone)	20-60 80-40
IV)	difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); 1,1,1,3,3-pentafluorobutane ( $\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3$ , HFC 365 mfc)	10-98 90-2
V)	difluoromethoxy	

	bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ );	10-40
	1,1,1,4,4,4-hexafluorobutane ( $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ , HFC 356 ffa)	90-60
VI)	difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ );	25-96
	methoxymethyl methylether	75-14
VII)	difluoromethoxy bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ );	35-98
	n-hexane	65-2
VIII)	1-difluoromethoxy 1,1,2,2-tetrafluoroethyl difluoromethyl ether ( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ );	25-93
	n-pentane	75-7
IX)	1-difluoromethoxy 1,1,2,2-tetrafluoroethyl difluoromethyl ether ( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ );	50-98
	dimethyl ketone (acetone)	50-2
X)	1-difluoromethoxy 1,1,2,2-tetrafluoroethyl difluoromethyl ether ( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ );	25-98
	n-hexane	75-2
XI)	1-difluoromethoxy 1,1,2,2-tetrafluoroethyl difluoromethyl ether ( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ );	10-98
	ethyl alcohol	90-2

- a 3. Use of azeotropic compositions according to ~~claims 1~~ <sup>Claim 1</sup>  
a ~~and 2~~ in correspondence of which an absolute minimum or  
maximum of the boiling temperature at the pressure of  
1.013 bar with respect to the pure products is noticed,  
defined as follows:

A) difluoromethoxy-bis

	(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); n-pentane	62% by wt. 38% by wt.
B)	difluoromethoxy- bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); iso-pentane	63% by wt. 36% by wt.
C)	difluoromethoxy- bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); dimethyl ketone (acetone)	42% by wt. 58% by wt.
D)	difluoromethoxy- bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); 1,1,1,3,3-pentafluorobutane ( $\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3$ , HFC 365 mfc)	60% by wt. 40% by wt.
E)	difluoromethoxy- bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); 1,1,1,4,4,4-hexafluorobutane ( $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ , HFC 356 ffa)	20% by wt. 80% by wt.
F)	difluoromethoxy- bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); methoxymethyl methyl ether	59% by wt. 41% by wt.
G)	difluoromethoxy- bis(difluoromethyl ether) ( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ ); n-hexane	75% by wt. 25% by wt.
H)	1-difluoromethoxy-1,1,2,2-tetra- fluoroethyl difluoromethyl ether ( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ ); n-pentane	61% by wt. 39% by wt.
I)	1-difluoromethoxy-1,1,2,2-tetra- fluoroethyl difluoromethyl ether ( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ ); dimethyl ketone (acetone)	79% by wt. 21% by wt.
L)	1-difluoromethoxy-1,1,2,2-tetra- fluoroethyl difluoromethyl ether ( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ ); n-hexane	74% by wt. 26% by wt.
M)	1-difluoromethoxy-1,1,2,2-tetra- fluoroethyl difluoromethyl ether ( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ );	95% by wt.

ethyl alcohol

5% by wt.

- a 4. Use as foaming agents of near azeotropic compositions according to ~~claims 1 and 2~~ <sup>claim 1</sup> essentially consisting of:

composition  
% by wt.

- |  |               |
|--|---------------|
| II) difluoromethoxy-bis(difluoromethyl ether)<br>( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ );<br>iso-pentane  | 1-99<br>99-1  |
| III) difluoromethoxy-bis(difluoromethyl ether)<br>( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ );<br>dimethyl ketone (acetone)   | 1-60<br>99-40 |
| IV) difluoromethoxy-bis(difluoromethyl ether)<br>( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ );<br>1,1,1,3,3-pentafluorobutane<br>( $\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3$ , HFC 365 mfc) | 1-99<br>99-1  |
| V) difluoromethoxy-bis(difluoromethyl ether)<br>( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ );<br>1,1,1,4,4,4-hexafluorobutane<br>( $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ , HFC 356 ffa) | 1-40<br>99-60 |
| VI) difluoromethoxy-bis(difluoromethyl ether)<br>( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ );<br>methoxymethyl methyl ether   | 1-96<br>99-14 |

wherein the difluoromethoxy-bis(difluoromethyl ether) part contains up to 40% by weight of 1-difluoromethoxy-1,1,2,2-tetrafluoroethyldifluoromethyl ether.

- a 5. Use as foaming agents of near azeotropic compositions according to ~~claims 1 and 2~~ <sup>claim 1</sup> essentially consisting of:

composition  
% by wt.

- |  |       |
|--|-------|
| IX) 1-difluoromethoxy-1,1,2,2-tetrafluoroethyl | 30-99 |
|--|-------|

difluoromethyl ether  
 $(\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H})$ ;  
 dimethyl ketone (acetone)

70-1

- X) 1-difluoromethoxy-1,1,2,2-tetrafluoroethyl  
 difluoromethyl ether  
 $(\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H})$ ;  
 n-hexane

15-99

85-1

wherein 1-difluoromethoxy-1,1,2,2-tetrafluoroethyl di-  
 fluoromethyl ether contains up to 40% by weight of di-  
 fluoromethoxy-bis(difluoromethyl ether).

6. Use as foaming agents of near azeotropic compositions  
 according to <sup>claim 1</sup>~~claims 1 and 2~~ essentially consisting of:

1

composition

% by wt.

- I) difluoromethoxy-bis(difluoromethyl  
 ether)  
 $(\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H})$ ;  
 n-pentane

1-95

99-5

- VII) difluoromethoxy-bis(difluoromethyl  
 ether)  
 $(\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H})$ ;  
 n-hexane

30-99

70-1

wherein difluoromethoxy-bis(difluoromethyl ether) con-  
 tains up to 50% of 1-difluoromethoxy-1,1,2,2-tetrafluoroethyl  
 difluoromethyl ether.

7. Use as foaming agents of near azeotropic compositions  
 according to <sup>claim 1</sup>~~claims 1 and 2~~ essentially consisting of:

1

composition

% by wt.

VIII) 1-difluoromethoxy-1,1,2,2-tetrafluoroethyl difluoromethyl ether  
( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ );  
n-pentane

1-93

99-7

X) 1-difluoromethoxy-1,1,2,2-tetrafluoroethyl difluoromethyl ether  
( $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ );  
n-hexane

15-99

85-1

wherein 1-difluoromethoxy-1,1,2,2-tetrafluoroethyl difluoromethyl ether contains up to 50% by weight of difluoromethoxy-bis(difluoromethyl ether).

8. Use as foaming agents of ternary near azeotropic compositions according to <sup>claim 1</sup>~~claims 1 and 2~~ essentially consisting of:

composition  
% by wt.

XII) difluoromethoxy-bis  
(difluoromethyl ether)  
( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ );  
1,1,1,3,3-pentafluorobutane  
( $\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3$ , HFC 365 mfc)  
hydrocarbon

1-64

98-1

1-35

XIII) difluoromethoxy-bis  
(difluoromethyl ether)  
( $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ );  
1,1,1,4,4,4-hexafluorobutane  
( $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ , HFC 356 ffa)  
hydrocarbon

1-22

98-43

1-35

9. Use of the compositions according to claim 8 wherein hydrocarbon is selected between n-pentane and isopentane.

10. Use of compositions according to <sup>claim 8</sup>~~claims 8 and 9~~ wherein

hydrocarbon is present in the range 1-20% by weight.

- a
11. Use of azeotropic or near azeotropic compositions according to <sup>claim 1</sup>~~claims 1-10~~ wherein the ether portion HFPE1 and/or HFPE2 can contain at least up to 10% by weight of hydrofluoropolyethers having the same structure but with boiling point in the range 5°-80°C.
  12. Use as foaming agents, for the preparation of polyurethanes, of the compositions according to <sup>claim 1</sup>~~claims~~  
~~1-7 and 11~~, mentioned at points I, II, IV, V, VI, VII, VIII, X, A, B, D, E, F, G, H and L.
  13. Use of the compositions according to claim 12 in amounts in the range 1-15% by weight on the total preparation, including the same foaming agent; preferably 1.5-10% by weight, more preferably 1.5-8% by weight on the total formulation for the foam preparation.
  14. Use of the compositions according to claim 12 in combination with H<sub>2</sub>O and/or CO<sub>2</sub>.
  15. Use of the compositions according to claim 14 wherein the water amount is in the range 0.5-7, preferably 1-6, and more preferably 1-4 parts by weight on one hundred parts of polyol.
  16. Use of the compositions according to claim 14 wherein the CO<sub>2</sub> amount is in the range 0.6-10 parts, preferably



1-8 parts by weight on one hundred parts of polyol.

a 17. Use of the compositions according to <sup>claim 1</sup> ~~claims from 1 to~~

a ~~16~~ wherein stabilizers for radicalic decomposition reactions are added, the concentration of which is in the range 0.1-5% by weight with respect to the foaming agent.

a 18. Use as foaming agents for thermoplastic polymers of the compositions according to <sup>claim 1</sup> ~~claims 1-11~~, mentioned at points I, II, III, VII, VIII, IX, X, XI, XII, XIII, A, B, C, G, H, I, L and M.

19. Use of the compositions according to claim 18 in combination with foaming agents of physical type selected from CO<sub>2</sub>, HFC 134a, HFC 227ea, HFC152a (1,1 difluoroethane), HFC 236ea (1,1,1,2,3,3 hexafluoropropane) or mixtures thereof.

20. Use of the compositions according to claims 18 and 19 in amounts in the range 5-30% by weight on the thermoplastic polymer.

21. Use of the compositions <sup>or</sup> according to claims from 1 to 11 and from 18 to 20 wherein stabilizers for radicalic decomposition reactions are added, the concentration of which is in the range 0.1-5% by weight with respect to the foaming agent.

SubB3 22. Polyurethane compositions comprising the foaming

44

claim 12

a

compositions according to ~~claims 12-17.~~

1

23. Compositions of thermoplastic polymers according to

claim 18

a

~~claims 18-21.~~

1

Add E5